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REVIEW

Combination of CuBr_2 and multi-functional ligand bearing a bidentate nitrogen unit, a phenol group and a TEMPO moiety as catalyst for the aerobic oxidation of primary alcohols

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KEYWORDS

Alcohols;
Aerobic oxidation;
Multifunctional ligand;
TEMPO;
Bidentate nitrogen ligand

Abstract A novel ligand (L) bearing a bidentate nitrogen ligand unit, a phenol group and a TEMPO moiety has been synthesized. The ligand has been used as a catalyst precursor for the copper-catalyzed aerobic oxidation of alcohols to aldehydes, in the presence of K_2CO_3 . The complex obtained *in-situ* from the ligand with copper(II) bromide (CuBr_2) in a 2:1 acetonitrile/water mixture, selectively catalyzes the aerobic oxidation of primary benzylic and allylic alcohols to their corresponding aldehydes, and no over-oxidation products are detected.

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1. Introduction

The oxidation of alcohols into aldehydes and ketones is an important transformation in organic chemistry (Larock, 1989; Mallat and Baiker, 2004; Sheldon et al., 2002). Traditional methods to carry out this reaction involve the use of stoichiometric amounts of inorganic oxidants, such as chromium(VI) oxide (Hudlicky, 1990; Sheldon and Kochi, 1984), MnO_2 or hypervalent iodine compounds (Alvarez et al., 1998; Dess and Martin, 1991, 1983; March, 1992; Paterson et al., 2003). In most cases, these oxidants are expensive, toxic, or hazardous. Therefore, the development of selective and environmentally friendly oxidations catalyzed by transition-metal complexes is a very important and topical area of contemporary catalysis. From the viewpoint of green chemistry, the best choice to replace the above oxidants is the employment of molecular oxygen or air as oxidant in the transformation of alcohols into aldehydes and ketones. Oxygen is atom efficient and produces water as the only by-product when being used as oxidant. However, the molecular oxygen is a triplet in its ground state and as such is inert toward substrate oxidation. Catalysts are thus required to use molecular oxygen as an oxidant. Many methods have been developed to activate oxygen to achieve this goal (Parmeggiani and Cardona, 2012). Copper seems to be an appropriate metal for the catalytic oxidation of alcohols with oxygen since it is present in nature as the catalytic center in a variety of enzymes (e.g. galactose oxidase) that catalyze this conversion (Whittaker et al., 1989; Whittaker and Whittaker, 1993). The crystal structure of galactose oxidase shows that the protein provides four ligands for the Cu(II) arranged in an unusual non-square-planar coordination (Ito et al., 1991, 1994): two tyrosine phenolates and two histidine imidazoles. Based on the structure Stack and his co-workers designed and prepared a [Cu(II)BSP] model (Fig. 1) of the mononuclear copper enzyme galactose oxidase (Wang et al., 1983). The model catalytically oxidized

benzylic and allylic alcohols to aldehydes with O_2 under mild conditions.

In 1984, Semmelhack and coworkers (Semmelhack et al., 1984) first reported a CuCl–TEMPO system for the aerobic oxidation of alcohols. The combination of CuCl and the stable nitroxyl radical, TEMPO (2,2,6,6-tetramethylpiperidinyloxy) is able to catalyze the aerobic oxidation of alcohols to the corresponding carbonyl compounds. Later, a number of [copper/TEMPO] based catalysts have proven to be highly efficient for the transformation of a broad range of alcohols to aldehydes and ketones (Betzemeier et al., 2000; Figiel et al., 2009; Gamez et al., 2003, 2004; Hoover and Stahl, 2011; Lu et al., 2008).

In 2003, Sheldon et al. (Dijksman et al., 2003; Gamez et al., 2003; Sheldon and Arends, 2004) reported that $[\text{CuBr}_2(2,2'\text{-bipyridine})]$ can catalyze the selective and very mild aerobic oxidation of primary alcohols to aldehydes in acetonitrile: water (2:1) in the presence of TEMPO and a base (tert-BuOK) as cocatalyst. The introduction of 2,2'-bipyridine can increase the solubility of the copper catalyst and provide beneficial electronic effects caused by the pyridine rings. Since then, many copper complexes of various nitrogen donor ligands in combination with TEMPO have been developed as catalysts for alcohol oxidation (Das and Paine, 2012; Hoover and Stahl, 2011; Kumpulainen and Koskinen, 2009; Ragagnin et al., 2002; Uber et al., 2007) and different mechanisms have been proposed (Cheng et al., 2010; Dijksman et al., 2003; Hoover et al., 2013; Michel et al., 2009; Semmelhack et al., 1984). Efficiency of TEMPO based catalytic systems leads to design of several ligand systems containing TEMPO unit backbone by Reedijk and his co-workers (Lu et al., 2008, 2009). The bpy/TEMPO-based molecules were used as catalyst precursors for the copper-catalyzed aerobic oxidation of alcohols to aldehydes and ketones, in the presence of tert-BuOK as co-catalyst. The complexes obtained *in-situ* from the ligands with copper(II) bromide in a 2:1 acetonitrile/water mixture, selectively catalyzed the aerobic oxidation of primary benzylic, allylic and aliphatic alcohols and secondary benzylic alcohols. However, functionalized 2,2'-bipyridine molecules are generally difficult to synthesize due to their structure characters. On the other hand, 2-pyridyl imines are easily available from the condensation of 2-pyridinecarboxaldehyde with primary amines and showed good performances as bidentate ligands in some metal catalyzed reactions (Chen et al., 2003; Qiu et al., 2009). We believe that 2-pyridyl imines can act as alternatives of 2,2'-bipyridine in the ligand systems containing TEMPO. Therefore, we have designed and synthesized a ligand bearing a bidentate nitrogen donor, a phenol group and a TEMPO moiety (Scheme 1). This ligand combined with CuBr_2 shows good catalytic performance in the oxidation of benzyl and allyl alcohols to their corresponding aldehydes with oxygen as oxidant.

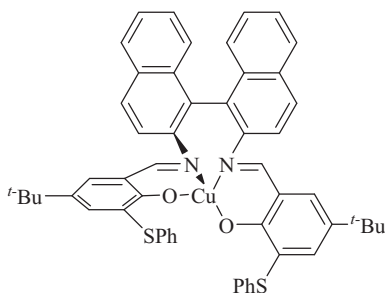
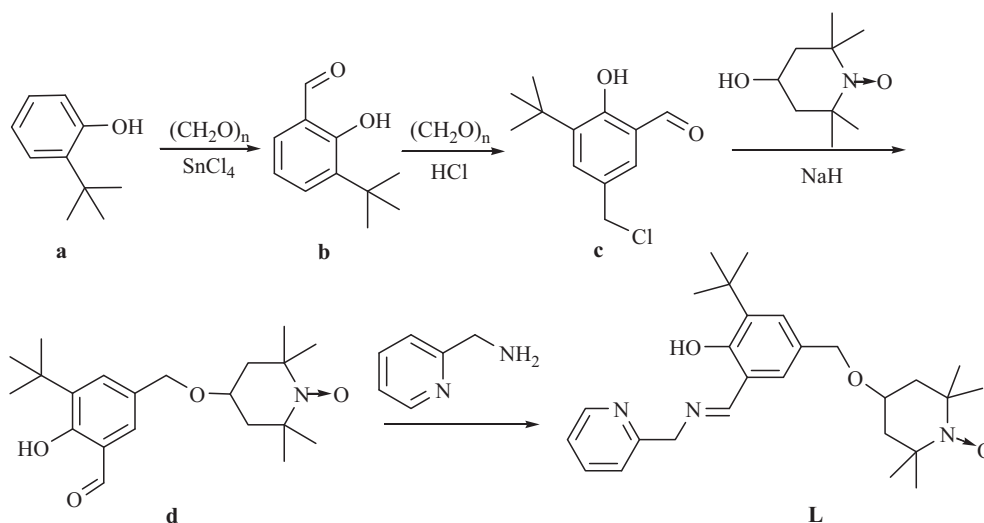


Figure 1 [Cu(II)BSP] model of the mononuclear copper enzyme galactose oxidase.

Scheme 1 Synthesis route for the model ligand **L**.

2. Experimental section

2.1. Materials and methods

2-tert-Butylphenol, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-OH-TEMPO), and 2-aminomethylpyridine were purchased from Acros Organics. Other chemicals were obtained from Tianjin Fuchen Chemical Reagent Factory, China. All the chemicals were used as received. The ¹H NMR spectra were recorded on a Bruker AC-P400 instrument using CDCl₃ or DMSO as solvent and TMS as internal standard. IR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets as the IR matrix. Melting points were determined on a Perkin XT-4 microscopic analyzer. ESI mass spectra were recorded on a LCQ advanced high-resolution mass spectrometer.

2.2. Synthesis of 3-tert-butyl-2-hydroxybenzaldehyde (**b**)

Compound **b** was synthesized according to reported procedures (Casiraghi et al., 1980). Light yellow liquid. Yield 7.4 g, 40%; ¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm): 11.79 (s, 1H; OH), 9.88 (s, 1H; CHO), 7.52 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H; CH), 7.39 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H; CH), 6.93 (t, *J* = 7.6 Hz, 1H; CH), 1.42 ppm (s, 9H; (CH₃)₃); ¹³C NMR (100 MHz, CDCl₃, TMS) δ (ppm): Arom-C: [161.22 (C), 138.22 (C), 134.11 (CH), 131.99 (C), 120.65 (CH), 119.22 (C)], tert-butyl C: [34.85 (CH₃), 29.20 (C)], 197.16 (CHO); IR (KBr): ν = 3447 (OH), 1653 (CHO) cm⁻¹.

2.3. Synthesis of 3-tert-butyl-5-(chloromethyl)-2-hydroxybenzaldehyde (**c**)

Intermediate **c** was prepared using the procedure reported in the literature (Kureshy et al., 2002; Minutolo et al., 1996). Light yellow crystalline solid. Yield: 7.5 g, 80%; m.p. 61–63 °C (lit. (Kureshy et al., 2002) 63–65 °C); ¹H NMR (400 MHz, DMSO, TMS) δ (ppm): 11.90 (s, 1H; OH), 9.98 (s, 1H; CHO), 7.74 (d, *J* = 2 Hz, 1H; CH), 7.63 (d, *J* = 2.4 Hz, 1H; CH), 4.81 (s, 2H; CH₂), 1.39 ppm (s, 9H; (CH₃)₃); ¹³C NMR (100 MHz,

CDCl₃, TMS) δ (ppm): Arom-C: [161.29 (C), 139.16 (C), 134.58 (CH), 131.80 (C), 128.27 (CH), 120.33 (C)], tert-butyl C: [34.96 (CH₃), 29.11 (C)], 196.77 (CHO), 45.92 (CH₂); IR (KBr): ν = 3448 (OH), 1652 (CHO), 1265 (CH₂) cm⁻¹.

2.4. Synthesis of intermediate (**d**)

Sodium hydride (0.52 g, 60% dispersion in mineral oil, 13 mmol) was suspended in dry THF (40 ml) under nitrogen at room temperature. To the suspension 4-OH-TEMPO (1.95 g, 11 mmol) was added. The mixture was stirred at room temperature for 3 hours. A solution of **c** (2.0 g, 8.8 mmol) in dry THF (35 ml) was added dropwise using a dropping funnel at 0 °C, then TBAI (0.075 g, 0.2 mmol) was added. The mixture was stirred at room temperature for 2 days. Methanol was added slowly and the reaction mixture was concentrated to give an oily residue. The residue was extracted with EtOAc, dried over anhydrous Na₂SO₄, and filtered. The filtrate was concentrated under reduced pressure and the residue subjected to silica gel column chromatography, eluting with a 20:1–15:1 (V:V) petroleum ether-EtOAc mixture. The eluent was evaporated in vacuum and the residue was recrystallized from petroleum ether to afford intermediate **d** as a red crystal. Yield: 3.19 g, 40%; m.p. 90–92 °C (from petroleum ether); IR (KBr): ν = 3363 (OH), 1646 (CHO), 1374 (N–O), 1217 (CH₂) cm⁻¹; HR-MS (ESI): *m/z*: calcd for C₂₁H₃₃NO₄: 364.2482 [M + H]⁺; found: 364.2486. (piperidine nitroxide abstracts hydrogen from water in the mass spectrometer source to give [M + 1]⁺ ions) (Morrison and Davies, 1970).

2.5. Synthesis of the ligand **L**

A solution of **d** (1.0 g, 2.7 mmol) in absolute ethyl alcohol (5 ml) was dropwise added to 2-aminomethylpyridine (0.45 g, 4.1 mmol) in absolute ethyl alcohol (5 ml) during 3–4 h. The mixture was poured into appropriate amount of 4 Å molecular sieves, and stirred at room temperature for 4 h. Then, it was filtered and the solvent was removed. The residue was extracted with petroleum ether. The extract was dried over anhydrous Na₂SO₄, and filtered. The filtrate was concentrated

to obtain **L** as an oily product. Yield: 1.2 g, 98%. IR (KBr): $\nu = 3418$ (OH), 1630 (C=N), 1361 (N-O), 1267 (CH₂), 765 (CH) cm⁻¹; HR-MS (ESI): m/z : calcd for C₂₇H₃₉N₃O₃: 454.3064 [M+H]⁺; found: 454.3060 (piperidine nitroxide abstracts hydrogen from water in the mass spectrometer source to give [M+1]⁺ ions) (Morrison and Davies, 1970).

2.6. Catalytic reaction

The aerobic oxidations of alcohols were performed in a 10 ml two-necked round bottomed flask equipped with a magnetic stirrer and a condenser, immersed in a temperature-controlled water bath. A balloon filled with oxygen was connected to the top of the condenser. In a typical experiment, the alcohol (2.0 mmol) was dissolved in a CH₃CN/H₂O (2:1) solvent mixture (3 ml). K₂CO₃ (41.4 mg, 0.3 mmol) was added, followed by the addition of CuBr₂ (22.3 mg, 0.1 mmol), resulting in a blue-green suspension. The ligand **L** (45.2 mg, 0.1 mmol) was added and the reaction suspension slowly turned dark-green. Samples of the reaction mixture were taken out regularly and analyzed by a Shandong Lunan Ruihong Gas Chromatograph (SP-6800A) equipped with a 30 m × 0.25 mm SE 30 capillary column and an FID detector.

3. Results and discussion

3.1. Synthesis and characterization of **L**

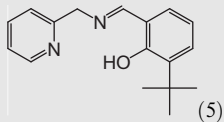
Herein, the multi-functional ligand **L** with a bidentate nitrogen donor, a phenol group and a TEMPO moiety, has been synthesized as shown in Scheme 1.

First, 3-tert-butyl-2-hydroxybenzaldehyde **b** was prepared from 2-tert-butylphenol with a moderate yield according to reported procedures (Casiraghi et al., 1980). The ¹H NMR characterization results are consistent with those in the literature (Wong et al., 2010). Chloromethylation of **b** with a reported procedure (Kureshy et al., 2002; Minutolo et al., 1996) produced a salicylaldehyde derivative 3-tert-butyl-5-(chloromethyl)-2-hydroxybenzaldehyde **c** which is the key intermediate for obtaining the model compound **L** due to its special structure. In the structure of **c** a chloromethyl group at C-5 and a carbonyl group can make it easier to react with 4-OH-TEMPO and 2-aminomethylpyridine successively to give **L**. In the processes to synthesize **L** condensation of **c** and 4-OH-TEMPO in the presence of NaH yielded intermediate **d**. Failure to record the ¹H NMR of **d** indicated the presence of the TEMPO being a radical in the structure of **d**. This combined with the HR-MS characterization result confirmed the successful synthesis of **d**. Finally, the model compound **L** was obtained in high yield by condensation of **d** and 2-aminomethylpyridine, which was characterized by FT-IR and HR-MS.

3.2. Catalytic performances

The oxidation of benzyl alcohol has been chosen as a model reaction to test the catalytic potential of the combination of CuBr₂-**L** for aerobic oxidations of alcohols. It has been known in the literature that the use of basic media leads to more efficient oxidation reactions of alcohols in various Cu/TEMPO systems (Gamez et al., 2003, 2004; Lu et al., 2008; Semmelhack

Table 1 [Copper/**L**]-catalyzed aerobic oxidation of benzyl alcohol to benzaldehyde.

Entry	Ligand (mol%)	CuBr ₂ (mol%)	K ₂ CO ₃ (mol%)	Conversion (%)
1	L (5)	5	0	1
2	L (5)	0	36	0
3	L (0)	5	36	0
4	L (5)	5	36	99
5	TEMPO (5)	5	36	3
6	 (5)	5	36	1

All the above mol% are versus the substrate. Selectivity always >99% based on GC.

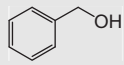
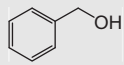
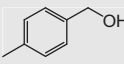
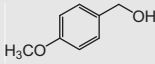
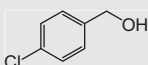
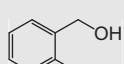
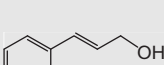
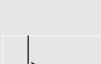
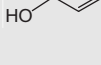
Conditions: Alcohol (2 mmol), MeCN (2 ml), water (1 ml), O₂ (balloon), 50 °C, reaction time 11 h.

et al., 1984). Therefore, the catalytic aerobic reactions have been performed in acetonitrile-water (2:1) under the conditions using 5 mol% of CuBr₂ together with 5 mol% of **L** as catalyst in the presence of K₂CO₃ (36 mol% of substrate). The results are listed in Table 1.

It is found that the reaction proceeded smoothly, and the quantitative aerobic conversion of benzyl alcohol to benzaldehyde is obtained at 50 °C under atmospheric oxygen pressure in 11 h (Table 1, entry 4). It should be noted that both **L** and CuBr₂ are essential for the observed catalysis, since no benzaldehyde is obtained in the absence of them. Besides, the beneficial use of base is evident from the lower yield of benzaldehyde in the absence of K₂CO₃ (Table 1, entry 1). As described in the literature (Gamez et al., 2003), the role of the base is probably to deprotonate the alcohol and, thus, favor the coordination of the resulting alcoholate to the copper species, increasing the activity. For comparative purposes, we have tested TEMPO, and another bidentate nitrogen ligand without the TEMPO moiety as reference mediators respectively, which leads to lower yields, i.e. less than 3% in the same conditions (Table 1, entries 5, 6), thus underlining the importance of the co-existence of TEMPO and bidentate nitrogen donor in the model compound **L**. After receiving these results, we have optimized the loading amount of K₂CO₃. The best result has been received when the molar ratio of K₂CO₃ to benzyl alcohol is 15 mol%. Therefore, the loading amount of K₂CO₃ is chosen as 15 mol% in the subsequent experiments.

On the basis of these results we then investigate the generality of the catalyst system with respect to the alcohol structure. It has been found that various types of primary benzylic alcohols, including those bearing both electron-withdrawing and electron-donating groups, have been quantitatively converted to the corresponding aromatic aldehydes under the optimal reaction conditions in 5 h (Table 2, entries 3–6). These results clearly demonstrate that electronic effects do not seem to have a significant effect on the reaction time and final product yields for electron-rich and electron-deficient benzylic substrates (Jiang and Ragauskas, 2006). However, it seems that the catalyst system is sensitive to steric effect. It is noted that longer reaction time is required to reach the same yield when comparing *o*-chlorobenzyl alcohol to *p*-chlorobenzyl alcohol as

Table 2 Oxidation of selected alcohols to corresponding aldehydes and ketones with the copper/**L**/base system.

Entry	Substrate	Temperature (°C)	Time (h)	Conversion (%)
1		25	6.5	51.2
2		50	6.5	99.5
3		50	5	99.2
4		50	5	99.3
5		50	5	99.4
6		50	9	99.4
7		50	2	99.4
8		50	4.5	99.4
9		50	7	0.6
10	1-Octanol	50	7	0

Conditions: Alcohol (2 mmol), CuBr₂ (5 mol%), MeCN (2 ml), catalyst **L** (5 mol%), water (1 ml), K₂CO₃ (15 mol%), O₂ (balloon). Selectivity always > 99% based on GC.

substrate. The catalyst system is very effective for the aerobic oxidation of allylic alcohols to the corresponding α , β -unsaturated aldehydes (Table 2, entries 7, 8). For instance, cinnamyl alcohol is selectively oxidized to cinnamaldehyde with a yield of 99.4% only in 2 h (Table 2, entry 7). However, the catalyst system shows poor performances in the oxidation of secondary benzyl alcohols and aliphatic alcohols. For instances, only 0.6% of acetophenone is received under the optimal reaction conditions in 7 h in case of 1-phenylethanol as substrate (Table 2, entry 9), and no product is detected in case of 1-octanol as substrate (Table 2, entry 10). These results were also observed in the other Cu-TEMPO based catalyst systems, which were ascribed to the steric hindrance of the methyl group of the secondary alcohol (Gamez et al., 2003).

On the basis of the catalytic results in combination with the structure of **L**, and the mechanism for galactose oxidase catalyzed oxidation of galactose (Gamez et al., 2004; Whittaker and Whittaker, 1993), especially the mechanisms for (Cu–N–ligand–TEMPO)-catalyzed oxidation of primary alcohols described in the literature (Cheng et al., 2010; Hoover et al., 2013) it is believed that a Cu^{II}-alkoxide complex as shown in Fig. 2 is generated *in-situ* from the coordination of **L** and alcohol with CuBr₂ in the catalytic cycle. Once the complex is formed, a hydrogen atom is abstracted from the Cu^{II}-alkoxide to give the aldehyde. Since the reaction takes place in homogeneous medium, two possible pathways may be present to complete this process. One is the abstraction of the hydrogen atom by the TEMPO moiety from the same complex, the other is the

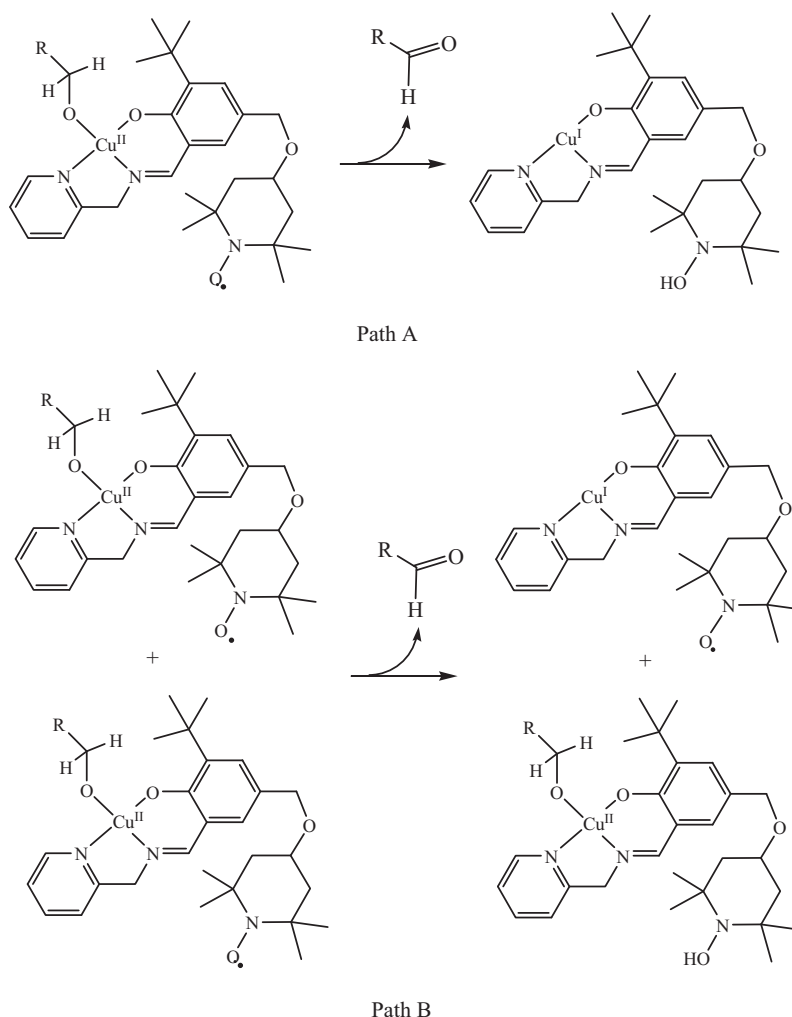


Figure 2 Possible pathways for the abstraction of hydrogen in the catalytic cycle.

abstraction of the hydrogen atom by the TEMPO moiety from the second complex. From the existing results and information it is difficult to determine whether the abstraction of the hydrogen is intramolecular or intermolecular.

4. Conclusion

A novel ligand bearing a bidentate nitrogen ligand unit, a phenol group and a TEMPO moiety has been designed and synthesized. The multifunctional ligand in combination with CuBr_2 has been used as catalyst for the aerobic oxidation of alcohols in the presence of K_2CO_3 as basic co-catalyst. The copper(II) complex generated *in-situ* from CuBr_2 and the ligand selectively catalyzes the aerobic oxidation of primary benzylic, and allylic alcohols to the corresponding aldehydes in acetonitrile/water (2:1).

Contributors

Yuecheng Zhang: Synthesis of the new ligand.

Mengjia Cui: Catalysis.

Wenchan Ma: Analysis.

Jiquan Zhao: Creation of the idea and design of the synthetic route.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2014.10.015>.

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